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Compounds of Uranium with the Transition Metals of the First Long Period*

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In the alloy systems of uranium with Mn, Fe, Co and Ni, the following compounds occur: U_6Mn, U_6Fe, U_6Co and U_6Ni, all tetragonal and isostructural, and of a new structural type; UCo, a body-centered cubic compound, $Z=8$, with a unique structure; UNi, structure undetermined; UMn_2, UFe_2 and UCo_2, with the C–15 structure; UNi_2, with the C–14 structure; UNi_5 with the $PdBe_5$ structure, closely related to the C–15 structure. In addition, UCu_5 has a similar structure.

Lattice constants and full structure determinations are reported for all compounds except UNi. For the latter, only powder data have been available, and the structure is complex.

Introduction

The transition elements Mn, Fe, Co and Ni, form several intermetallic compounds with uranium, ranging in composition from U_6M to UM_5. In general, the compounds formed by these four metals with uranium are very similar. Also included in this paper is the structure of UCu_5, isostructural with UNi_5.

Some attempt has been made, without appreciable success, to interpret the bonding in these structures by Pauling's rules and metal valences (Pauling, 1938, 1947). It seems noteworthy that uranium, as well as other heavy metals, form few or no compounds with chromium, and that the number of compounds increases rather regularly with atomic number at least until nickel is reached. Metallic valences neither of Pauling nor of Hume-Rothery (1926) and Mott & Jones (1936) are helpful in understanding this behavior.

A comprehensive study of the phase systems of uranium with manganese, iron, cobalt, nickel and copper has been made by combined X-ray, optical and thermal studies. The complete phase diagrams will be published elsewhere (vol. 19 of Div. 5 of National Nuclear Energy Series), but without a detailed account of the structures of the phases found.

U_6M compounds

Occurrence of U_6M *compounds*

Peritectic compounds of the composition U_6M were found in the alloy systems of uranium with manganese, iron, cobalt and nickel.‡ Fortunately, alloys containing 70–90 atomic % uranium occasionally provided single crystals in the form of needles which could be separated from the matrix mechanically or chemically. In samples containing an excess of the transition element the eutectic matrix was preferentially dissolved by dilute acids. The needles remaining after this treatment were only slightly pitted.

Unit-cell dimensions

Single crystals of the four isostructural alloys, U_6Mn, U_6Fe, U_6Ni and U_6Co, were examined by the single-crystal rotation and oscillation methods, and powder diagrams were obtained from powdered single crystals. The compounds crystallize in a body-centered tetragonal lattice with the lattice constants given in Table 1. The lattice constants reported are those obtained from the powder diagrams. The reported densities were calculated for four units of U_6M per unit cell.

Table 1. *Lattice constants of* U_6M *compounds*

	a (A.)	c (A.)	ρ(g.cm.$^{-3}$)
U_6Mn	$10{\cdot}29\pm0{\cdot}01$	$5{\cdot}24\pm0{\cdot}02$	17·8
U_6Fe	$10{\cdot}31\pm0{\cdot}04$	$5{\cdot}24\pm0{\cdot}02$	17·7
U_6Co	$10{\cdot}36\pm0{\cdot}02$	$5{\cdot}21\pm0{\cdot}02$	17·7
U_6Ni	$10{\cdot}37\pm0{\cdot}04$	$5{\cdot}21\pm0{\cdot}02$	17·6

The composition of the phase

The probable composition of U_6M was first obtained from the volume of the unit cell, the atomic volume of uranium, and the atomic volume of the transition metal by assuming the validity of Mehl's modification of Vegard's law (Mehl & Mair, 1928). Subsequently, when it was discovered that relatively large amounts of single crystals were available, the needles were analyzed chemically. The formula of the cobalt compound determined by chemical analysis was $U_6Co_{1{\cdot}09}$. (A similar result was obtained with the manganese compound.) The cobalt content is high, undoubtedly owing to the fact that the needles were separated from a cobalt-rich alloy. For this composition the volume of the unit cell requires four U_6M per unit cell.

Laue symmetry and intensity estimation

Single-crystal rotation diagrams were taken of U_6Fe, U_6Mn, U_6Co and U_6Ni with the axis of rotation normal

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‡ U_6Fe was first reported by Kaufmann, Cullity & Gordon (1943), and U_6Ni by Foote, Clark, Cieslicki, Nelson & Lane (1945).

to (001) to obtain ($hk0$) and ($hk1$) data. In addition, a single crystal of U_6Co was rotated about an axis normal to (110) to obtain (hhl) data. Oscillation diagrams taken about the needle axis, together with Laue diagrams taken normal to the needle axis, indicated planes of symmetry normal and parallel to the fourfold axis. The Laue symmetry is, then, D_{4h}.

The intensities were estimated visually from the single-crystal rotation diagrams by comparison with known intensities. Absorption corrections were made for each ($hk0$) reflection by evaluating the integral $\int_A e^{-\mu S}da$, assuming that the crystal was bathed in a beam of parallel radiation. S is the distance travelled by the X-ray beam through the crystal in scattering from the elemental area da; μ is the absorption coefficient. The cross-section of the crystal was square, and because of the high absorption coefficient ($\mu = 6200$ cm.$^{-1}$) and the size of the crystal (square edge $= 0{\cdot}003$ cm.) the calculations were greatly simplified. Absorption corrections were much more difficult to make for ($hk1$) reflections and were assumed to be those for the corresponding ($hk0$) reflection. Absorption rendered the (hhl) data less suitable for use in the determination of parameters.

Determination of the space group

The absences noted may be described as follows:

hkl with $h+k+l$ odd, $0kl$ with k and l odd.

The combination of the requirement of four transition metal atoms per unit cell and the presence of reflections of the type (hhl) with $l = 2n$, eliminated all space groups except D_{4h}^{18}, D_{4h}^{17}, D_4^9, C_{4v}^{10}, C_{4v}^{9}, D_{2d}^{11}, D_{2d}^{10} and D_{2d}^{9}. The twenty-four uranium atoms were considered to be arranged in either three eightfold positions or in a sixteenfold and an eightfold position. Positions of these types which led to uranium–uranium spacings of $\frac{1}{2}c$ were discarded, as the required U–U distance would then be abnormally small (2·61 A.). The following positions remain (nomenclature of the *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, rev. ed., Band 1):

D_{4h}^{18}	16k	8h
D_{4h}^{17}	16l	8h, 8i, 8j
D_4^9	16k	8h, 8i, 8j
C_{4v}^{10}	16d	8c
C_{4v}^{9}	16e	8c, 8d
D_{2d}^{11}	16j	8f, 8g, 8i
D_{2d}^{10}	16i	8e, 8h
D_{2d}^{9}	16j	8j, 8h, 8i

Since all of the positions listed above belong to the same plane group, $C4ll$, a plot of the structure factor, F, as a function of x and y was made for one-sixteenth of the unit cell using Lipson & Beevers strips. (This evaluation is similar to the one suggested by Bragg & Lipson, 1936.) The plots were made for the strong reflections (550), (11,5,0), (660), (10,6,0), (510) and for the absent reflections (12,2,0), (12,0,0), (880), and (770). ((12,2,0) and (12,0,0) were later observed as weak on a much more intense diagram taken with the crystal rotating about [010].) The maximum value of F on the plot was rated as 100. It was assumed that parameter values (x, y) which led to $|F| < 20$ for sixteenfold positions could not possibly account for the strong reflections regardless of the contribution of atoms in the eightfold position. Similarly, values of (x, y) which gave $|F| > 80$ for the sixteenfold position could not become absent reflections regardless of the contribution of atoms in the eightfold position. Eliminating parameter values for the sixteenfold position on this basis, using the maxima mentioned above, led to the following possible (x, y) parameter values (where $x = y$ the parameters correspond to eightfold positions):

	x	y		x	y
A	0·183	0·017	D	0·100	0·100
B	0·183	0·167	E	0·067	0·033
C	0·083	0·083	G	0·217	0·100

Parameters A and B do not lead to a suitable arrangement; C and D correspond to eightfold positions. The value E is impossible because it places the uranium atoms too close together. Using the parameters, G, a reasonable arrangement of uranium atoms was obtained as well as a rough agreement with the intensity data. When the uranium atoms in the sixteenfold position have the G parameter values, one, and only one, of the eightfold positions was favored by intensity calculations. A reasonable value for the x parameter for the uranium atoms in the eightfold positions seemed to be either 0·100 or 0·400, corresponding to D. These parameters gave very reasonable agreement with the intensity data.

A Fourier projection on (001) (Fig. 1), using the signs of F's determined by the parameters above, gave the positions and parameters listed below. Recalculation of the F's using the new parameters did not require the change in sign of any term used in the Fourier series. Thus, the parameters listed below are the best that can be obtained from a Fourier projection.

$4\,M$ at $(0,0;\ \tfrac{1}{2},\tfrac{1}{2}) + (0,0;\ 0,0)$,

$16\,U_I$ at $(0,0;\ \tfrac{1}{2},\tfrac{1}{2}) + (x,y;\ \bar{x},\bar{y};\ \bar{x},y;\ x,\bar{y};$
$\bar{y},x;\ y,\bar{x};\ y,x;\ \bar{y},\bar{x})$
with $x = 0{\cdot}2141$, $y = 0{\cdot}1021$,

$8\,U_{II}$ at $(0,0;\ \tfrac{1}{2},\tfrac{1}{2}) + (x,\tfrac{1}{2}+x;\ \bar{x},\tfrac{1}{2}-x;\ \tfrac{1}{2}+x,\bar{x};\ \tfrac{1}{2}-x,x)$
with $x = 0{\cdot}4068$.

The ratio of the average heights of the peaks due to the uranium atoms to that of the two M atoms is 92/55 after correction for the valleys in the Fourier projection. Since the plot was made from intensity data from U_6Mn, the ratio should be approximately 92/50. The Fourier projections were made with several sets of intensity values obtained by using different absorption corrections. The parameters obtained were the same in each case within several ten-thousandths of a parameter unit. Although the absorption factor does not seem important to the determinations of the parameter values in the Fourier method, the agreement between calculated and observed intensities is very dependent on the absorption factor.

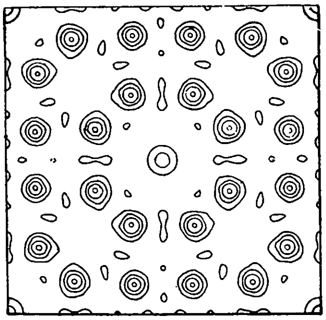

Fig. 1. Fourier projection of U_6Mn on (001).

The amplitude data, treated by the least-squares method due to Hughes (1941), gave the parameters $x=0{\cdot}2134$, $y=0{\cdot}1065$ for the sixteenfold positions and 0·4053 for the eightfold position. A third more or less trial-and-error refinement gave 0·213, 0·103 and 0·405. It is difficult to say which set of parameters gives the best agreement with the intensity data. The first and last sets of parameters permit more reasonable U–U distances. Only one least-square determination was performed, which may explain the higher value for the y parameter obtained by that method. The parameter values determined from the Fourier projection are used in Table 2, where calculated and observed intensities for the ($hk0$) data are compared. An artificial temperature factor was used to bring the data into agreement over the whole range of the film.

The above positions eliminate space groups D_{4h}^{17}, D_{2d}^{9}, D_{2d}^{11} and C_{4v}^{9}, since the sixteenfold positions in these space groups put atoms impossibly close together in the same plane. Most of the eightfold positions are eliminated for similar reasons. The decision between the remaining space groups depends upon the arrangement in the z direction.

Table 2. *Intensity comparisons for* U_6Mn: ($hk0$) *data*

Indices	$I_{\text{calc.}}$	$I_{\text{obs.}}$
110	28·3	*
200	3·3	15
220	29	32
310	31·7	32
400	89·7	60
330	102	100
420	120	120
510	336	200
440	49	50
530	22·3	20
600	186	75
620	16·4	15
710	4·7	900
550	1290	
640	66·6	100
730	19	50
800	1·6	—
820	12·6	15
660	214	185
750	25·7	40
840	79·2	70
910	23·4	25
930	61·4	65
770	4	5
10,0,0	149	190
860	8	
10,2,0	7·4	10
950	44·8	35
10,4,0	32·1	30
11,1,0	150	160
880	8·1	—
11,3,0	1·3	50
970	86·3	
10,6,0	417	400
12,0,0	1·4	—
11,5,0	1160	850
12,2,0	9·9	—
12,4,0	60·6	60
990	317	170

* Not observed on this film because of the beam catcher. It has been observed on other films in about the right magnitude.

There are only four different arrangements in the z direction, all of which are very close to the arrangement in space group D_{4h}^{18}. In this space group two uranium atoms in the sixteenfold position are placed only 2·69 A. apart. The arrangement in C_{4v}^{10} does not permit an enlargement of this distance, and there seems to be no other reason for considering this set of positions further. The arrangements in D_{2d}^{10} and D_{4}^{9} both permit this distance to be enlarged, since the z parameter allows variation from the parameterless positions in D_{4h}^{18}. There is an optimum value of this parameter which places the two uranium atoms a maximum distance apart (2·73 A. in each case), with $z=0{\cdot}042$ for D_{2d}^{10} and $z=0{\cdot}208$ for D_{4}^{9}. Increasing or decreasing the value of this z parameter places two uranium atoms closer together.

It should be possible to distinguish among these four possibilities and to determine the z parameter on the basis of the ($00l$), (hkl) or ($0kl$) data. Unfortunately, here, as in the case of the ($hk0$) data, the absorption factor is very important, and it is even more difficult to calculate. However, it has been carefully calculated for ($00l$) data. From the comparison of the estimated and calculated intensities given in Table 3, it appears that the z parameter must differ less than 0·02 from the ideal values of 0 and $\frac{1}{4}$ for D_{2d}^{10} and D_{4}^{9} respectively. The temperature factor has been omitted in these calculations; if it is appreciable, it will require the parameter to differ even less from the ideal values.

Table 3. *Calculated and observed intensities for* U_6Mn: ($00l$) *data*

Indices	$I_{\text{calc.}}$			$I_{\text{obs.}}$
	$z=0{\cdot}00$	$z=0{\cdot}02$	$z=0{\cdot}04$	
002	606	680	1030	630
004	260	260	260	260
006	242	186	59	195

With this small variation it becomes difficult to choose between the arrangements in D_{4}^{9} and D_{2d}^{10}. The arrangement in D_{2d}^{10} seems more probable because it does not permit the reflections of the type ($0kl$) with k and l odd to occur at all. These reflections are not observed. In fact, since the parameter seems near zero, it is quite possible that the arrangement in D_{4h}^{18} is correct. Intensities have been calculated for the (hkl) reflections on the basis of the D_{4h}^{18} arrangement, using the absorption correction cited previously, and are given in Table 4. The agreement is only fair; the discrepancies are undoubtedly due to the approximate absorption correction.

A list of interatomic distances for the D_{4h}^{18} arrangement is given in Table 5. The shortest U–U distance corresponds to a 1·8 bond using Pauling's rule relating bond distance to bond number. However, this distance

Table 4. *Calculated and observed intensities for* U_6Mn: *(hk1) data*

Indices	$I_{calc.}$	$I_{obs.}$	Indices	$I_{calc.}$	$I_{obs.}$
101	0	—	831	627	500
211	0·6	—	901	0	—
301	0	—	921	23	75
321	858	900	961	52	
411	32	40	851	6·8	20
501	0	—	941	17·7	—
431	34	60	10,1,1	0·51	—
521	2·7	20	10,3,1	19	35
611	45	50	871	454	250
541	0·2	--	961	30	25
631	0·3	—	11,0,1	0	—
701	0	—	11,2,1	11·3	15
721	85	100	10,5,1	5·7	
651	2·8	—	11,1,1	132	100
811	1·5	15			
741	3·6				

Table 5. *Interatomic distances in* U_6M *compounds*

($a = 10{\cdot}34$ A., $c = 5{\cdot}21$ A.)

U_I ligands		U_{II} ligands		M ligands	
Ligand	Distance (A.)	Ligand	Distance (A.)	Ligand	Distance (A.)
1 U_I	2·69	1 U_{II}	2·73	2 M	2·61
2 M	2·78	2 U_I	2·84	8 U_I	2·78
1 U_{II}	2·84	4 U_{II}	3·24		
2 U_I	3·08	4 U_I	3·28		
2 U_{II}	3·28	2 U_I	3·39		
2 U_I	3·35				
1 U_{II}	3·39				
2 U_I	3·47				

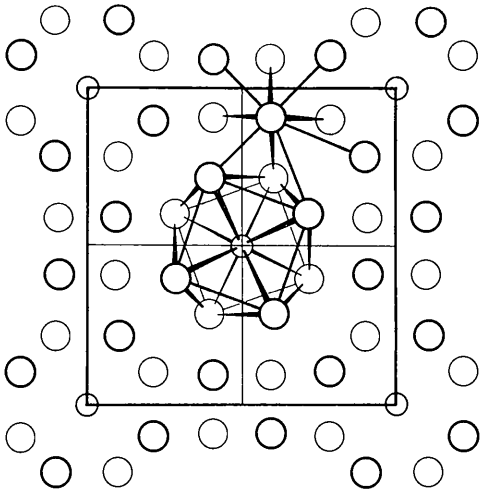

Fig. 2. The U_6M structure. Large circles are uranium, small are transition atoms. Width of line indicates position along c_0. Since all uranium atoms lie on mirror planes parallel to (001), for any atom below (or above) a uranium atom there is a corresponding atom above (or below). The configurations about transition atoms and U_{II} atoms (eightfold set) are indicated by shaded interatomic links.

is only 0·07 A. shorter than the shortest U–U distance in α-uranium (Jacob & Warren, 1937), and the number of short distances is lower in U_6M. Calculating the bond numbers for all bonds to U_I and U_{II} neighbors and M neighbors, the valences for U_I and U_{II} are 5·46 and 5·36, while that for M is 4·50. This is probably in not too unreasonable agreement with the expected value of 5·78 for uranium (Pauling, 1947), though in rather poor agreement with the same expected value for the transition metals.

In the structure M atoms form chains parallel to c_0, and each is at the center of a square antiprism of uranium atoms (Fig. 2). The square above the M atoms is rotated through 51° with respect to the square below, instead of an ideal 45°.

The eightfold uranium atoms, U_{II}, are in an essentially body-centered environment of uranium atoms (Fig. 2), in which the surrounding cube of uranium atoms is stretched along c_0. Instead of six next-nearest octahedral neighbors, each U_{II} has five near neighbors in the (001) plane, three at shorter distances than in the surrounding cube of uraniums, while the two above and below this plane are at much greater distances.

If one considers planes of uranium atoms at $z=0$, or $z=\frac{1}{2}$ (given different weight circles in Fig. 2), one sees that the arrangement tends to be a square net, deformed by Mn atoms at $z=\frac{1}{4}$, $\frac{3}{4}$. The nets at $z=0$ and $z=\frac{1}{2}$ are staggered with respect to each other. The structure appears to be based on a simple body-centered arrangement of uranium atoms, rather highly deformed.

U*M* compounds

Only two compounds of composition U*M* exist in the alloys of uranium with manganese, iron, cobalt, nickel and copper. These are UNi and UCo. The structure of UCo has been determined, but that of UNi appears to be too complex to interpret on the basis of the powder data available.

UCo crystallizes in a body-centered cubic lattice with a lattice constant, $a_0 = 6{\cdot}3557 \pm 0{\cdot}0004$ A. The X-ray density is 15·37 g.cm.$^{-3}$ with eight UCo groups per unit cell.

Structure determination

The only systematic absences observed are those required of a body-centered lattice. This observation and the general extinction requirements of the cubic space groups permit only four structures, three based on space group T_d^3 and one on space group T^5. The positions available in T_d^3 are also available in T^3.

Structures based on T_d^3:

I 8 U at $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + (x,x,x;\ x,\bar{x},\bar{x};\ \bar{x},x,\bar{x};\ \bar{x},\bar{x},x)$,
8 Co at $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + (x,x,x;\ x,\bar{x},\bar{x};\ \bar{x},x,\bar{x};\ \bar{x},\bar{x},x)$.
II 8 U at $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + (x,x,x;\ x,\bar{x},\bar{x};\ \bar{x},x,\bar{x};\ \bar{x},\bar{x},x)$,
6 Co at $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + (0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0)$,
2 Co at $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + (0,0,0)$.
III Interchange uranium and cobalt positions in II.

Structures based on T^5:

IV 8 U at $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + (x,x,x;\ \frac{1}{2}+x,\frac{1}{2}-x,\bar{x};\ \bar{x},\frac{1}{2}+x,\frac{1}{2}-x;\ \frac{1}{2}-x,\bar{x},\frac{1}{2}+x)$,
8 Co at $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) + (x,x,x;\ \frac{1}{2}+x,\frac{1}{2}-x,\bar{x};\ \bar{x},\frac{1}{2}+x,\frac{1}{2}-x;\ \frac{1}{2}-x,\bar{x},\frac{1}{2}+x)$.

Structure III is immediately eliminated by the intensity data as it requires that reflections with all even indices be the strongest maxima present.

Two-dimensional plots of $\sqrt{(FF^*)}$ for the reflections (110), (200), (220) and (310) were made for all possible values of the uranium and cobalt parameters with the aid of Beevers–Lipson strips. For structures I and II it was impossible to find values of the parameters which would permit the observed intensities. For structure IV additional plots were made for the reflections (400), (420), (440), (620), (640) and (800). By comparison of these plots it was found that a fairly large region of uranium and cobalt parameters would satisfy the observed intensities; the cobalt parameter, particularly, had a large degree of freedom.

Intensities were calculated for all reflections for nine pairs of uranium and cobalt parameter values in the permitted region. By general comparison, and by specific comparisons of (422) and (322); (322) and (420); (514) and (622); (611), (532) and (620); (316) and (444), the parameter value can be limited to $x=0{\cdot}0347\pm0{\cdot}0015$ for uranium, and $x=0{\cdot}294\pm0{\cdot}003$ for cobalt. Intensities calculated using these parameters are given in Table 6.

Table 6. *Comparisons of intensity for the* UCo *structure*

hkl	$I_{\text{calc.}}$	$I_{\text{obs.}}$	*hkl*	$I_{\text{calc.}}$	$I_{\text{obs.}}$
110	4	5	600, 442	29	10
200	41	60	611, 532	81	110
211	22	17	620	7	5
220	138	140	514	126	132
310	80	77	622	11	5
222	32	35	316	60	30
312	69	65	444	31·5	5
400	30	27	710, 550, 534	278	300
411, 330	19	14	640	7	Abs.
420	48	52	712, 633, 552	460	475
332	69	75	642	129	65
422	71	82	730	137	107
510, 134	145	137	732, 516	789	827
512	148	137	800	18	Abs.
440	15	5	118, 714, 554	1190	1000
433, 530	73	107			

Interatomic distances

The structure of UCo is a distorted CsCl arrangement. In an ideal CsCl arrangement with the same unit-cell dimensions, each uranium atom would have eight equidistant cobalt neighbors at 2·75 A. In addition, there would be six uranium atoms at a distance of 3·18 A.

In the distorted structure the eight cobalt neighbors have been split up into four groups at four different distances: 1 at 2·65, 3 at 2·81, 1 at 2·86 and 3 at 2·88 A. The six uranium neighbors have been split into two groups of three: 3 at 2·77 and 3 at 3·64 A. The reason for this distortion is not apparent.

Table 7. *Interatomic distances in* UCo

Atom	No. of neighbors	Kind of neighbor	Distance (A.)
U	3	U	2·772
U	3	U	3·645
U	1	Co	2·654
U	3	Co	2·809
U	1	Co	2·855
U	3	Co	2·875
Co	3	Co	2·677
Co	3	Co	3·779
Co	1	U	2·649
Co	3	U	2·809
Co	1	U	2·855
Co	3	U	2·875

UM_2 compounds

Unit cell and lattice constants

The intermetallic compounds, UMn_2, UFe_2 (Kaufmann, Cullity & Gordon, 1943) and UCo_2 crystallize in a face-centered cubic lattice. The lattice constants, determined from back-reflection precision powder diagrams, are listed in Table 8 together with the X-ray densities. Cobalt was found to be soluble in UCo_2 by metallographic methods. Chemical analysis placed the limit of the solubility at approximately 72 atomic % cobalt. The lattice constant of a 75 atomic % cobalt alloy was examined as a function of quenching temperature to get an independent estimate of the solubility (Table 9). The difference in the volume of the unit cell for pure UCo_2 and that found for the solubility limit at 1000° C. is 9·8 A.^{3} This volume change corresponds to the replacement of one uranium atom by one cobalt atom. The solubility limit of cobalt in UCo_2 at 1000° C. is, on this interpretation, 70·8 atomic % cobalt, in good agreement with the chemical result.

Table 8. *Lattice constants of* UM_2 *compounds*

	a (A.)	ρ(g.cm.$^{-3}$)
UMn_2	$7{\cdot}1628\pm0{\cdot}0014$	12·57
UFe_2	7·058 (Kaufmann *et al.*, 1943)	13·21
UCo_2	$6{\cdot}9924\pm0{\cdot}0004$	13·83

Table 9. *Lattice constant of* 75 *atomic* % *cobalt alloy as function of quenching temperature*

Quenching temperature (° C.)	Lattice constant (A.)
1000	6·9272
900	6·9309
800	6·9352
Pure UCo_2	6·9924

Structure

These intermetallic compounds are isostructural with $MgCu_2$, the *C*–15 structure type (*Strukturbericht*, 1931*a*). In this structure there is a diamond arrangement of uranium atoms, and tetrahedra of transition atoms within the tetrahedral interstices of the uranium network. The structure is parameterless; therefore, only crude intensity calculations have been made for one of these compounds. Lorentz, polarization, temperature and absorption factors have been omitted. These intensity comparisons are given in Table 10. A list of nearest neighbors is given in Table 11.

Table 10. *Observed and calculated intensities for* UMn_2

hkl	$I_{obs.}$	$I_{calc.}$	*hkl*	$I_{obs.}$	$I_{calc.}$
111	*vw*	471	531	*w*	1580
200	0	0	600, 442	0	0
220	*ms*	2855	620	*m*	3120
311	*s*	7150	533	*mw*	2650
222	*vw*	328	622	0	505
400	*vw*	384	444	0	304
331	*w*	1057	551, 711	*mw*	1010
420	0	0	640	0	0
422	*ms*	4050	642	*ms*	4180
333, 511	*ms*	4500	731, 553	*s*	5310
440	*m*	3550	800	*mw*	1080

Table 11. *Interatomic distances in* UM_2 *compounds*

Atom	No. of neighbors	Kind of neighbors	Distance (A.)		
			UMn_2	UFe_2	UCo_2
U	4	U	3·101	3·056	3·028
U	12	*M*	2·970	2·926	2·899
M	6	*M*	2·532	2·495	2·472
M	6	U	2·970	2·926	2·899

Unit cell and structure of UNi_2

UNi_2 is unique in that it is not isomorphous with the alloys above, but crystallizes in a hexagonal lattice with unit-cell dimensions $a_0=4{\cdot}966$, $c_0=8{\cdot}252$ A., $\rho=13{\cdot}46$ g.cm.$^{-3}$. The arrangement of the atoms in the unit cell is identical with that of $MgZn_2$, the *C*–14 structure type (*Strukturbericht*, 1931*b*). The atoms occur in the following positions:

4 U at $(\pm\frac{1}{3},\frac{2}{3},z;\ \frac{1}{3},\frac{2}{3},\frac{1}{2}-z)$ with $z=0{\cdot}056\pm0{\cdot}003$,

2 Ni_I at $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2})$,

6 Ni_{II} at $\pm(x,x,\frac{1}{4};\ 2x,x,\frac{1}{4};\ x,2x,\frac{1}{4})$ with $x=\frac{5}{6}$.

Intensity calculations were made, based on this structure. In order to allow (204), (116) and (222) to appear in proper relation to their immediate neighbors it was necessary to shift the z_U parameter from the ideal $\frac{1}{16}$ to 0·056. No variation of the nickel parameter was attempted, as its variation does not affect the intensities seriously. The intensity data were secured from powder diagrams by visual estimation, and thus further refinement of the parameters is unwarranted.

Table 12. *Intensity comparisons for* UNi_2

hkl	I_{calc}	$I_{obs.}$	*hkl*	$I_{calc.}$	$I_{obs.}$
001	0	—	302	1810	*m*
100	144	*w*	106	165	*m*+
002	152	*w*	205	2351	
101	110	*w*	214	40	—
102	326	*w*+	303	0	—
003	0	—	220	1807	*m*
110	1660	*s*	221	0	—
111	0	—	116	104	*vw*
103	2250	*s*	310	149	*vw*
200	459	*w*	222	391	*w*
112	3140	*s*	311	98	*w*
201	1240	*m*	007	0	
004	237	*w*	304	38	
202	2·5	—	206	455	*s*
104	39	—	215	1596	
113	0	—	312	300	*vw*
203	357	*w*	107	612	*vw*+
005	0	—	223	0	—
210	195	*w*	313	2100	*s*
211	129	*w*	305	0	—
114	54	*vw*	400	228	*vw*
105	1080	*m*	401	538	*w*
212	393	*w*	117	0	
204	42	*vw*	224	613	
300	930	*m*	216	287	*w*−
301	0	—	402	10	—
213	2700	*s*	207	30	*w*−
006	176	*w*	314	33	
115	0	—			

Table 13. *Interatomic distances for* UNi_2

	No.	Neighboring atom	Distance (A.)
U	1	U	3·201
	3	U	3·011
	3	Ni_{II}	2·903
	6	Ni_{II}	2·954
	3	Ni_I	2·903
Ni_I	6	U	2·903
	6	Ni_{II}	2·512
	2	Ni_I	4·126
Ni_{II}	2	Ni_I	2·512
	4	Ni_{II}	2·483
	2	*M*	2·903
	4	*M*	2·954

The intensity comparison and a list of nearest neighbors appear in Tables 12 and 13.

Lattice constant of UFeNi

The alloy UFeNi has been found to crystallize with the $MgCu_2$ (*C*–15) structure. The lattice constant of UFeNi is $a_0=7{\cdot}054\pm0{\cdot}001$ A. That of UFe_2, as determined by this laboratory, is $a_0=7{\cdot}0592\pm0{\cdot}0005$ A.

UM_5 compounds

The compounds UNi_5 and UCu_5 have been found in these systems. These compounds are isostructural with each other and with the compounds $PdBe_5$, $AuBe_5$ (Misch, 1935). The face-centered cubic cell dimensions are:

For UNi_5 $a_0=6{\cdot}7830\pm0{\cdot}0005$ A.,

For UCu_5 $a_0=7{\cdot}033\pm0{\cdot}002$ to $7{\cdot}038\pm0{\cdot}001$ A.

There is a slight solubility of uranium in the UCu_5 structure.

The structure of these phases is closely related to that of the parameterless $MgCu_2$ structure. Half of the uranium atom positions are regularly replaced by nickel or copper atoms, and four units of UCu_5 are required per unit cell. The structure may be thought of as a CaF_2 type in which half the F positions are filled by single nickel or copper atoms, half by tetrahedra of nickel or copper. This change necessitates a lower symmetry and a different space group, Td^2 or T^2 versus O_h^7, O^4 or T_h^4 for the $MgCu_2$ structure. The set of sixteenfold positions now available has but one parameter which is ideally $\frac{5}{8}$. Any variation in this parameter results in poorer intensity agreement and less satisfactory interatomic distances for both UNi_5 and UCu_5.

The following face-centered positions describe the structure:

4 U at $(0,0,0)$,

4 M_I at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$,

16 M_{II} at $(x,\bar{x},\bar{x};\ \bar{x},x,\bar{x};\ \bar{x},\bar{x},x;\ x,x,x)$; with $x=\frac{5}{8}$.

Intensity comparisons and interatomic distances are given in Tables 14 and 15.

Table 14. *Observed and calculated intensities for* UNi_5

Indices	$I_{\text{calc.}}$	$I_{\text{obs.}}$	Indices	$I_{\text{calc.}}$	$I_{\text{obs.}}$
111	22·4	*m*	600	10·5	*m*−
200	23·8	*m*	442	41·9	
220	131·6	*s*	620	114·1	*m*
311	331·6	*vs*	533	158·9	*m*+
222	78·3	*m*	622	113·1	*m*
400	1	Abs.	444	2·7	—
331	40·6	*m*	711	41·6	*m*
420	54·6	*m*+	551	41·6	
422	143·4	*s*	640	53·9	*m*
511	188·1	*s*+	642	315	*s*
333	62·7		731	486·8	*vs*
440	60·8	*m*	553	243·4	
531	63·7	*m*			

Table 15. *Interatomic distances in* UM_5 *compounds*

			Distance (A.)	
Atom	No. of neighbors	Kind of neighbors	UNi_5	UCu_5
U	12	U	4·81	4·97
U	4	*M*	2·95	3·05
U	12	*M*	2·83	2·92
M	12	*M*	2·83	3·05
M	6	*M*	2·40	2·49
M	4	U	2·95	3·05
M	3	U	2·83	2·92

X-ray methods

Rotation diagrams were made with a single-crystal camera of 5 cm. radius. Oscillations were over a 20° range. Powder diagrams were obtained from powder cameras of 5 and 5·73 cm. radius. When lattice constants are reported to more than three significant figures, the data are from diagrams made in a symmetrical, self-focusing, back-reflection camera manufactured by the Wyland Co. The data obtained were treated by the method of Cohen (1935). Nickel-filtered Cu $K\alpha$ radiation was used for all of the diagrams, and wave-lengths used were in true Ångström units rather than kX. units (Bragg, 1947).

Densities were calculated from the equation

$$\rho = 1{\cdot}6602\, M/V.$$

Unless otherwise stated the intensities were calculated using the following formula: $I \propto FF^*LPMA$, where F is the structure factor, F^* its complex conjugate, L the Lorentz factor, P the polarization factor, M the multiplicity factor and A the absorption factor. The temperature factor was usually omitted. As a consequence, reflections differing greatly in $\sin\theta$ should not be compared.

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